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Characterization of very low defect-density free-standing GaN Substrate Grown by Hydride-Vapor-Phase-Epitaxy.

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ABSTRACT
Structural, electrical and optical properties of free-standing 200-μm thick GaN films grown by hydride vapor phase epitaxy (HVPE) have been investigated. After laser lift-off, the GaN substrates were mechanically polished on both Ga and N-sides and dry etched only on the Ga-side to obtain a smooth epi-ready surface. Hot H_3PO_4 chemical etching on both surfaces was used to reveal the defect sites, which appeared as hexagonal pits. The etched surfaces were then examined by atomic force microscopy. A few seconds of etching was sufficient to smooth the N-face surface and produce etch pits with a density of $\approx 1x10^7$ cm^{-2}. In contrast, a 50 minute etching was needed to delineate the defect sites on the Ga-face which led to a density as low as $5x10^5$ cm^{-2}. From plan-view and cross-sectional transmission electron microscopy (TEM) analysis, we have estimated that the dislocation density is less than about $5x10^6$ cm^{-2} and $\approx 3x10^7$ cm^{-2} for the Ga and N-faces respectively. The full-width at half-maximum (FWHM) of the symmetric (0002) X-ray diffraction rocking curve was 69 and 160 arcsec for the Ga and N-faces, respectively. That for the asymmetric $(10\bar{1}4)$ peak was 103 and 140 arcsec for Ga and N-faces, respectively. Hall measurements demonstrated very high mobility (1100 and 6800 cm^2/V·s at 295 and 50 K, respectively) and very low concentration of donors ($2.1x10^{16}$ cm^{-3}) and acceptors ($4.9x10^{15}$ cm^{-3}). In the photoluminescence (PL) spectrum taken at 10 K, a rich excitonic structure has been observed with the highest peak attributed to the exciton bound to neutral shallow donor (BDE). The FWHM of the BDE peak was about 1.0 meV on the Ga face before and after hot chemical etching, whereas that on the N-face decreased from about 20 to 1.0 meV after chemical etching owing to the removal of the surface damage originated from the mechanical polishing.

INTRODUCTION
Recent developments in blue light emitting diodes, lasers, UV detectors, and high-temperature and high power transistors utilizing the III-nitride materials have led to intense demands on the quality of nitride semiconductors [1]. For high performance and longevity, devices require material with low extended and point defect density. Nitride semiconductors have been deposited by hydride vapor phase epitaxy (HVPE), organometallic vapor phase epitaxy (OMVPE) and by molecular beam epitaxy (MBE) on many different substrates. Despite progress, nitride semiconductors contain many structural and point defects which are undoubtedly caused by commonly used lattice mismatched substrates and that are believed to be

responsible for the high threshold-current required to achieve lasing in diodes and electronic devices not being par with performance expectation. Many of these problems would be alleviated considerably if native substrates were available. A possible approach is the growth of a quasi-bulk GaN film by high growth rate HVPE technique, which is capable of growing hundreds of microns thick films in a time-efficient manner [2, 3, 4]. Damage-free separation techniques are available to remove the sapphire substrate and obtain a free-standing GaN film which can then be mechanically polished to obtain a smooth surface for GaN homoeptaxial growth [5, 6]. We have investigated the structural, electrical and optical properties of free-standing 200-µm thick GaN films grown using HVPE technique.

EXPERIMENTAL DETAILS

The GaN samples were grown by HVPE on sapphire substrate to a thickness of 300 µm. In order to obtain a free-standing GaN substrate, the GaN films were then thermally decomposed at the film/substrate interface and lifted off by scanning a laser beam (with photon energy slightly larger than the GaN bandgap) from the back of sapphire. The GaN wafers were then mechanically polished and dry etched on the top Ga-face to obtain a smooth epi-ready surface, whereas the bottom N-face was only mechanically polished. The final thickness of the free-standing GaN substrate was about 200 µm. To determine the defect density, wet chemical etching was performed in hot phosphoric acid (H_3PO_4) on both Ga and N-faces of the sample [7, 8]. X-ray diffraction investigation was carried out in a Philips MRD high-resolution system equipped with a four-crystal Ge monochromator. Variable temperature Hall effect measurements were performed in dark between 50 and 300K using a Van der Pauw geometry. Ohmic contacts were formed with Ti/Al/Ti/Au metallization followed by rapid thermal annealing at 900 °C for 30s to the Ga-face of the n-type GaN. Variable temperature photoluminescence measurements were carried out in the range of 10 - 300 K on both the Ga and N-faces before and after the removal of what was presumably the damaged surface layer in wet chemistry.

RESULTS AND DISCUSSION

As received surfaces were examined by AFM imaging. The morphology of the mechanically polished and dry etched top Ga-face is shown in Fig. 1(a). A very smooth surface is observed except the scratch lines from mechanical polishing. The root mean square (rms) roughness of the Ga surface is 0.44 nm. Figure 1(b) shows an AFM image of the only mechanically polished N-face of the GaN substrate. Because the N-face was not dry etched, the rms roughness (6.1 nm) is much higher than that of the Ga-face. Again, lines from the mechanical polishing are visible on the surface, though to a lesser degree than on the Ga surface.

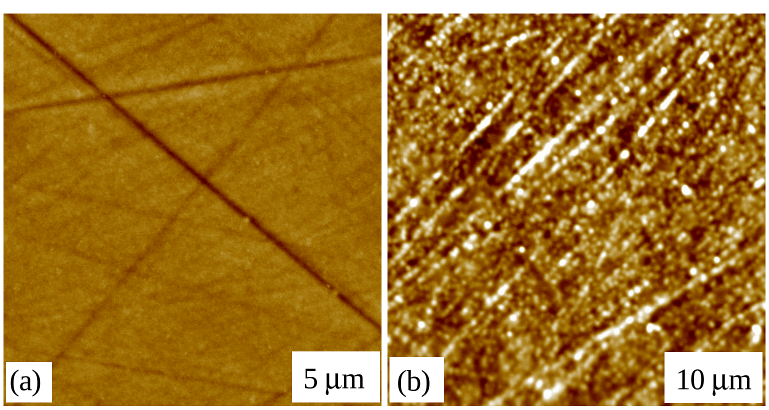

Figure 1. AFM images of the mechanically polished and dry etched Ga face (a), and the only mechanically polished N face (b) of the GaN substrate. The lines visible in (a) e (b) result from the mechanical polishing. The vertical scale varies between 0 and 10 nm in (a) and between 0 and 30 nm in (b).

Most of the structural defects originate from the heteroeptaxial nature of GaN growth on sapphire substrate. It has been found that in thick HVPE-grown GaN samples, the density of structural defects as a function of growth thickness declines significantly after a thickness of 75 μm [9,10]. To investigate structural defects on both Ga- and N-faces hot H_3PO_4 chemical etching was used to form etch pits at the surface defect sites. The N-face was etched in H_3PO_4 for only 15 seconds at 160°C, and the etched surface is shown in the AFM image of figure 2(a). After the etching, the rough and disordered surface has been smoothed (rms roughness = 1.9 nm), and the defect sites have been etched, revealing hexagonal pits. By counting the etch pits on several images, we ascertain that the density on the N-face is about 1×10^{7} cm^{-2}.

We have found that hot H_3PO_4 strongly attacks the N-face of GaN whereas the etch rate for the Ga-face is considerably lower. This creates a problem when etching the Ga-face to reveal the defects in that it is possible to etch through the sample from the N-face. This is especially a problem when the sample is of high quality, as it will take a long time to etch defect sites. To solve this problem, we used the surface tension of the acid to float the sample with the Ga-face down, minimizing the effects of the acid on the N-face. The morphology of the Ga-face etched with this method for 50 min is depicted in figure 2(b). The total density of etch pits on the Ga-face is about 5×10^{5} cm^{-2}, a value that is more than one order of magnitude lower than that found on the N-face.

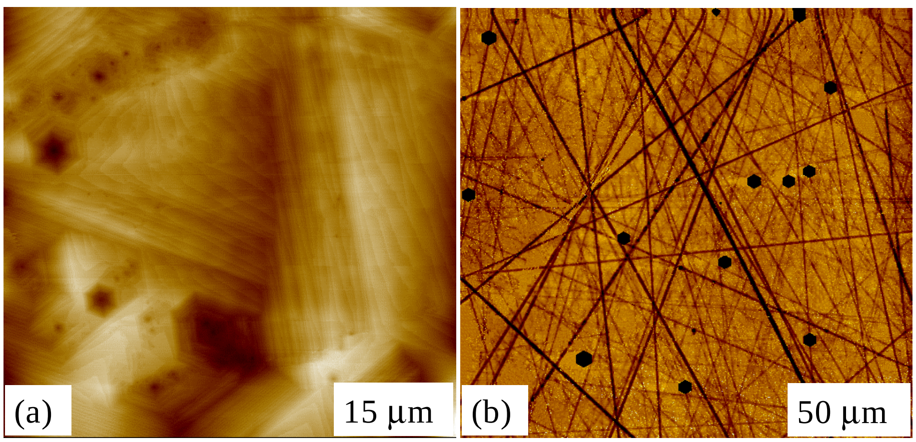

FIG. 2 (a) AFM image of the N face morphology after etching in H_3PO_4 for 15 seconds at 160°C. The rough surface imaged before the etching has been smoothed. Etch pits at the defect sites are formed with a density of $\sim1\times10^{7}$ cm^{-2}. The vertical scale varies between 0 and 15 nm. (b) AFM image of the Ga face etched for 50 min at 160°C in H_3PO_4. The lines from the mechanical polishing are still visible on the surface, indicating that the non-defective GaN has not been significantly etched. The EPD is $\sim5\times10^{5}$ cm^{-2}. The vertical scale varies between 0 and 20nm.

Additionally, the free-standing GaN template was studied using transmission electron microscopy (TEM) in order to estimate the effective dislocation density and to compare these values with densities found by defect revealing wet etching. Threading dislocations (mainly of mixed Burger's vectors) were found below the N-terminated surface. Their density determined from both plan-view and cross-sectional studies was about 3×10^{7} cm^{-2}, which compares well with the value of $\approx 1 \times 10^{7}$ cm^{-2} obtained from defect revealing etches. Only occasional dislocations were found in the plan-view sample on the Ga-terminated surface. Based on the plan-view study, the dislocation density was estimated to be less than 1×10^{7} cm^{-2}, however due to the very low statistics there is a relatively large uncertainty for this estimation. In cross-sectional study we could not find any threading dislocation within the electron transparent area and based on this information we estimated that the dislocation density is less than 5×10^{6} cm^{-2}.

Defect revealing chemical etching indicated a density of about 5×10^5 cm^{-2} for the top Ga face, which is in remarkable agreement with the value estimated from cross-sectional TEM analysis. The significantly lower dislocation density on the Ga-face side with respect to that near the N-face was probably due to dislocation interaction within the layer.

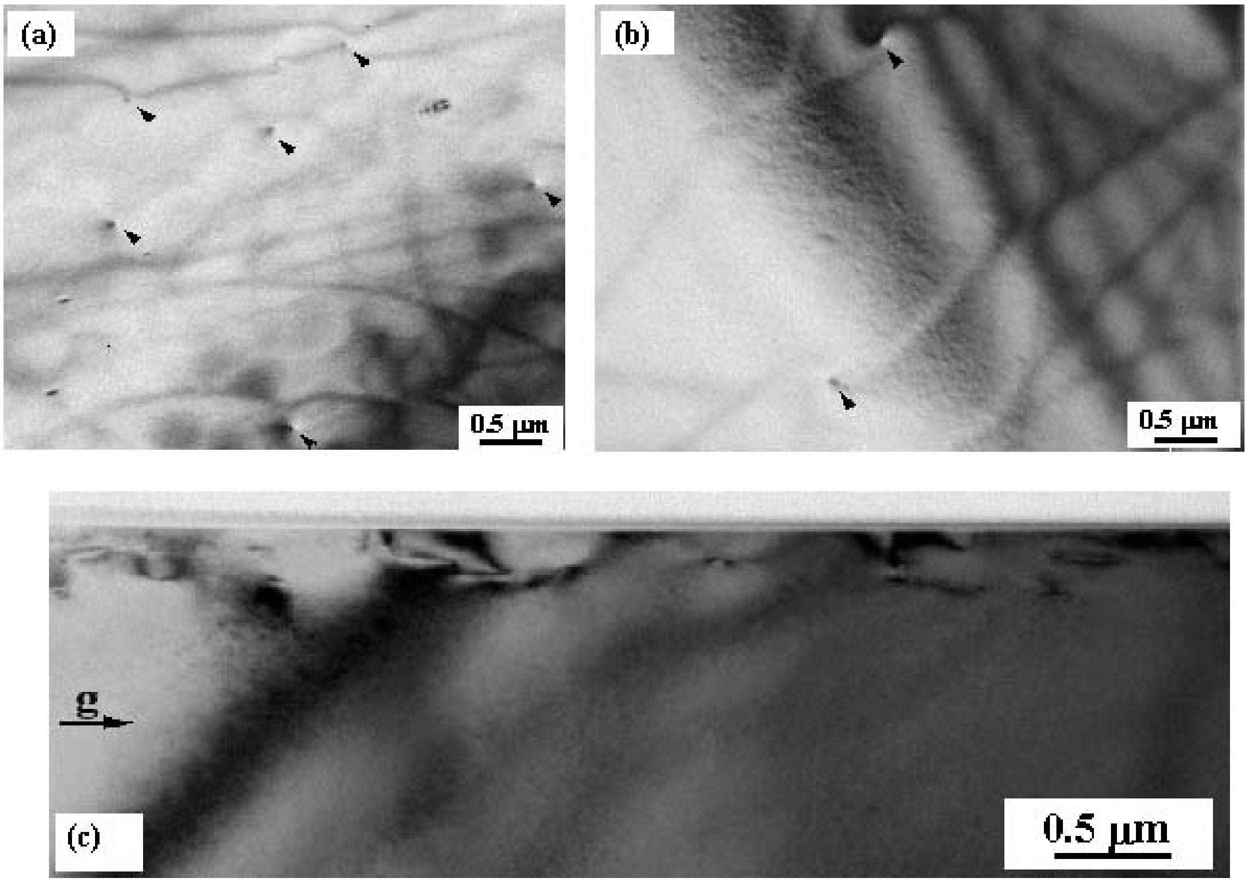

FIG. 3 Bright-field TEM micrograph of a plan-view GaN sample prepared for the N-face (a) and Ga-face (b), respectively. Visible edge-on dislocations are marked with arrows. We have estimated the dislocation density to be about 3×10^7 cm^{-2} and less than about 1×10^7 cm^{-2} for the N- and Ga-terminated surfaces, respectively. (c) Cross-sectional TEM image of the free-standing GaN substrate below the Ga-terminated surface. We have not found any threading dislocation within the electron transparent area and based on this information we have estimated that the dislocation density below the Ga-surface is less than 5×10^6 cm^{-2}.

The full-width-at-half-maximum (FWHM) of the symmetric (0002) X-ray diffraction rocking curve peak was 69 arcsec for the Ga-face and 160 arcsec for the N-face. The FWHM of the asymmetric $(10\bar{1}4)$ peak was 103 arcsec for Ga-face and 140 arcsec for the N-face. The difference in the XRD measurement of the two types of polarities, mainly the (0002) peak, suggests different defect structure and surface preparation.

Transport properties were investigated by variable temperature Hall measurements on the Ga-face, both as-prepared and with N-face etched some, in a temperature range from 50 to 350 K [11]. To etch the N-face of the free-standing thick GaN film, the sample was floated on hot H_3PO_4 acid until about 15 µm were etched. For as-prepared GaN, Hall mobilities of 1100 cm^2/V-s and 6800 cm^2/V-s were obtained at room temperature and 50 K, respectively. For GaN with N-face etched, Hall mobilities improved to 1200 cm^2/V-s and 7600 cm^2/V-s at room temperature and 50 K, respectively.

Additionally, we have studied the optical properties of the freestanding GaN layer by photoluminescence (PL) excited with He-Cd laser (λ=325 nm, excitation density ~ 0.1 W/cm^2). Figure 4 shows the low-temperature PL spectra in the range 3.2-3.5 eV, obtained from Ga and N faces of the sample. The PL spectrum from Ga- face was similar before and after the wet etching and demonstrated very sharp lines in the excitonic region. In contrast, PL from the N-face which was originally only mechanically polished, essentially revealed broadened exciton peak with the maximum at about 3.47 eV and FWHM of ~20 meV. After an H_3PO_4- based etching, the PL spectrum from the N-face became nearly identical to that of the original Ga-face (Fig. 4). The peaks observed at 3.4710 eV and 3.4778 eV are attributed to exciton bound to a neutral shallow donor (BDE) and free exciton (FE), respectively. The FWHM of these peaks at 10 K is about 1.0 and 2.5 meV, respectively. We assign the sharp peak at 3.4465 eV to exciton bound to a deep acceptor (BAE), yet it is deeper than usually observed BAE peaks. In the range 3.0 - 3.4 eV, we observed peaks related to excitonic transitions involving one to three LO phonons, as well as weak peaks due to shallow donor-acceptor pair (DAP) transitions.

In the range 2-3 eV, the PL spectrum at low excitation intensity revealed broad bands related to deep defects. A bright luminescence in the yellow-green region of spectrum was observed at room and low temperatures. Interestingly, the position of the band was quite different when the PL was observed from Ga and N-faces (Fig. 5). The green and yellow color of the PL from Ga and N faces, respectively, could be easily detected by naked eye. After etching, the position and shape of this band became nearly identical for both faces of the sample. The volume of the studied sample is almost free of dislocations (~5×10^5 cm^{-2}), whereas on the N-face (which was close to the sapphire/GaN interface) the dislocation density is higher (~1×10^7 cm^{-2}). Etching of the N- surface removed a few tens of microns, which were the most defective. The drastic improvement of the excitonic spectrum of N-face after wet etching may be related to etching of the defective material, as well as due to the removal of the surface damage.

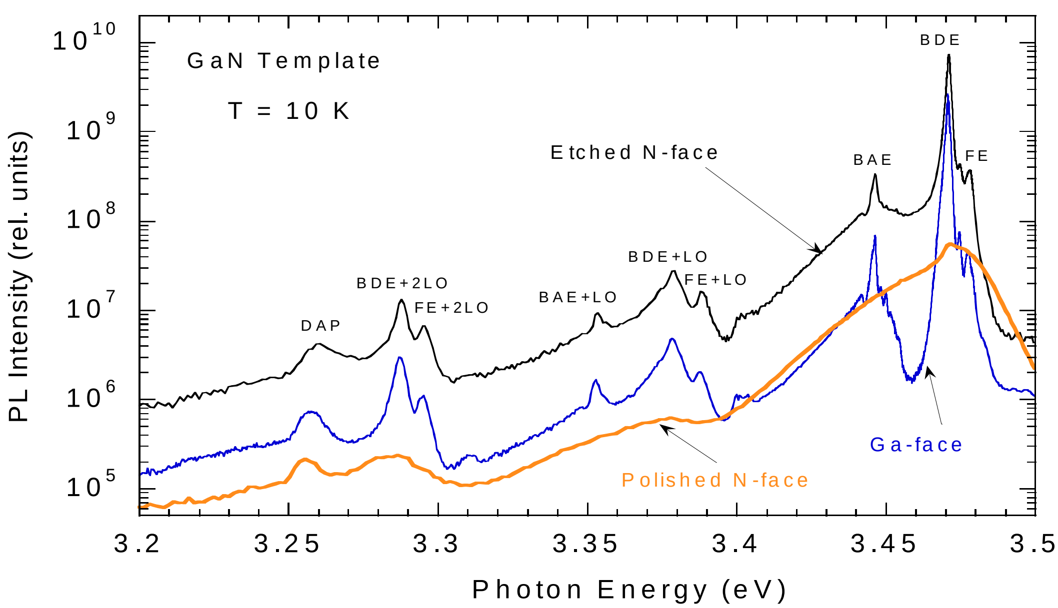

FIG. 4 PL spectrum of free-standing GaN sample in the excitonic region at 10 K for the N-face before and after hot wet etching and for Ga-face before etching. The FWHM of the BDE peak was about 1.0 meV on Ga face before and after hot chemical etching, whereas that on the N-face decreased from about 20 to 1.0 meV after chemical etching owing to the removal of the surface damage originated from the mechanical polishing.

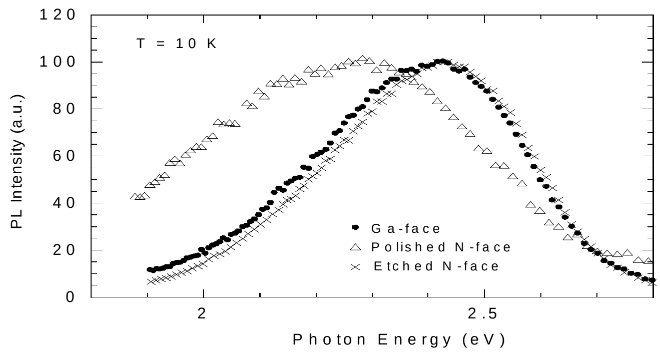

FIG. 5 Normalized PL spectrum in the range 1.9-2.8 eV at 10 K.

CONCLUSIONS

We have investigated the structural, electrical and optical properties of a free-standing GaN template grown by HVPE. The defect concentrations on Ga and N-faces were about 5×10^5 cm^{-2} and $\approx 1 \times 10^7$ cm^{-2}, respectively, as revealed by wet hot H_3PO_4 etching and TEM analysis. The FWHM of the (0002) X-ray diffraction peak was 69 and 160 arcsec for the Ga and N-faces, respectively. That for the $(10\bar{1}4)$ peak was 103 and 140 arcsec for Ga- and N-faces, respectively. After chemically etching the N-face to remove the damage caused by the mechanical polishing procedure, the PL spectra from the Ga- and N-faces were similar, with the N-face being slightly stronger, and exhibited a donor bound exciton linewidth of about 1 meV.

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